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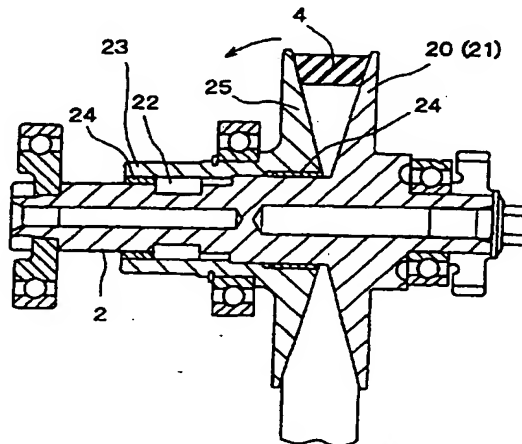Mitsuru Sugita

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(54) Abstract Title
Plain bearing with resin layer containing PTFE on both the sliding surfaces between the shaft and element of the bearing
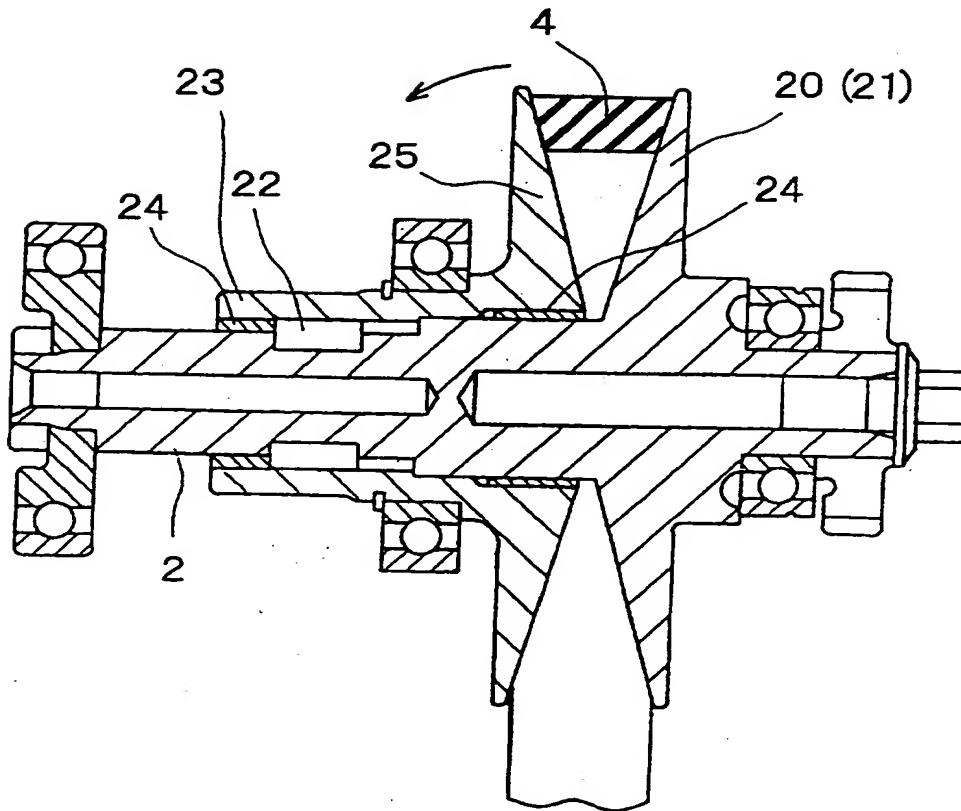
(57) A bearing structure with low coefficient of friction and high wear resistance comprising a shaft (2) coated with a resin composition containing polyamideimide (PAI) and 5 to 50% by weight of polytetrafluoroethylene (PTFE), and bearings (24) coated with a resin composition containing polyether ether ketone (PEEK) and not more than 50% by weight of PTFE. Alternatively, the resin compositions on the surfaces of the shaft and bearings may comprise PTFE in the respective above compositions and at least one member from the following resins: epoxy, phenol, polyamideimide, polyimide, polyacetal, polyamide, polyphenylene sulphide (PPS), PEEK or tetratluoroethylene-perfluoroalkylvinyl ether copolymer (PFA). Potassium titanate and/or a lead compound may be added to the resin. The application of this bearing structure to a continuously variable transmission is disclosed.

FIG.2

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This print incorporates corrections made under Section 117(1) of the Patents Act 1977.

FIG.1

FIG.2

BACKGROUND OF THE INVENTION

1) Field of the Invention

The present invention relates to a bearing structure, which comprises a shaft and a bearing for supporting the shaft, the shaft and the bearing having a resin layer formed on the respective sliding surfaces.

2) Related Art

Bearings having a resin layer formed on their sliding surfaces by coating are well known, and it is also well known that addition of polytetrafluoroethylene (which will be hereinafter referred to as PTFE) to the resin can reduce the coefficient of friction and also can improve the wear resistance, but their development has been based on a bearing structure comprising a metallic shaft and a resin-coated bearing.

Recent bearings have a tendency to be used in a severer condition, therefore they are required to have bearing structures with a higher wear resistance, etc. However, bearings having the resin layer on the sliding surfaces still have such problems as an unsatisfactory wear resistance and easy wear.

SUMMARY OF THE INVENTION

The present inventors have found that further reduction in the coefficient of friction and further

improvement of wear resistance can be attained by coating both of the shaft sliding surface and the bearing sliding surface with resin and adding a specific amount of PTFE to the resin, and have established the present invention.

The first aspect of the present invention provides a bearing structure, which comprises a shaft and a bearing for supporting the shaft, the shaft and the bearing having a resin layer formed on the respective sliding surfaces, the resin layer on the shaft sliding surface being made from a resin composition comprising at least one member selected from the group consisting of epoxy resin, phenol resin, polyamideimide resin, polyimide resin, polyacetal resin, polyamide resin, polyphenylene sulfide resin, polyether ether ketone resin and tetrafluoroethylene-perfluoroalkylvinyl ether copolymer resin and 5 to 50% by weight of PTFE based on total resin composition, and the resin layer on the bearing sliding surface being made from at least one member selected from the group consisting of epoxy resin, phenol resin, polyamideimide resin, polyimide resin, polyacetal resin, polyamide resin, polyphenylene sulfide resin, polyether ether ketone resin and tetrafluoro-ethylene-perfluoroalkylvinyl ether copolymer resin and not more than 50% by weight of PTFE based on total resin composition.

DETAILED DESCRIPTION OF THE INVENTION

The resin for use in the resin layer on the shaft and bearing sliding surfaces includes, for example, epoxy

resin, phenol resin, polyamideimide resin, polyimide resin, polyacetal resin, polyamide resin, polyphenylene sulfide resin, polyether ether ketone resin and tetrafluoroethylene-perfluoroalkylvinyl ether copolymer

5 resin, which are all distinguished in wear resistance.

In the ordinary bearing structure, shaft exchange is hard to be made, whereas bearing exchange is easy to be done. Thus, it is desired to make the wear resistance of shaft sliding surface higher than that of bearing sliding

10 surface, thereby making the wear rate of shaft sliding surface as low as possible. To this effect, it is desirable that the resin layer on the shaft sliding surface is made from a thermosetting resin having a high hardness and that on the bearing sliding surface from a thermoplastic resin

15 having a relatively low hardness and a low friction property (the second aspect of the present invention).

The thermosetting resin for use in the resin layer on the shaft sliding surface includes, for example, epoxy resin, phenol resin, polyamideimide resin and polyimide

20 resin. When at least one of these resins contains PTFE, the friction resistance can be lowered and the wear resistance can be improved. Less than 5% by weight of PTFE, no satisfactory effects can be obtained, whereas more than 50% by weight of PTFE the wear resistance is lowered on the

25 contrary. Thus, the PTFE content must be 5 to 50% by weight and particularly a content of 10 to 30% by weight thereof is preferable because of their more remarkable effects.

The thermoplastic resin for use in the resin layer

on the bearing sliding surface includes, for example, polyacetal resin, polyamide resin, polyphenylene sulfide resin, polyether ether ketone resin, thermoplastic polyamideimide resin, thermoplastic polyimide resin and

5   tetrafluoroethylene-perfluoroalkylvinyl ether copolymer resin. When at least one of these resins contains PTFE, the friction resistance can be further lowered and the wear resistance can be improved. More than 50% by weight of PTFE the wear resistance is lowered on the contrary. Thus, the

10   PTFE content must be not more than 50% by weight, and particularly a content of 10 to 30% by weight thereof is preferable because of their more remarkable effects.

When the shaft or the backing metal of bearing is made of a metal, and the resin may be bonded directly to the

15   shaft or the bearing surface, the bonding force between the shaft or the bearing surface and the resin is not satisfactory in some cases. As disclosed in JP-A-57(1982)-74153, it has been already established as a technique to set a metallic mesh or bronze powder to the backing metal surface of the

20   bearing by sintering and cover the metallic mesh or bronze powder layer with a resin by filling or impregnation, thereby assuring the bonding force. This means that, for further improvement of bearing sliding surface, it will be possible to use various means, for example, addition of a lead compound

25   to the resin layer (the fourth aspect of the present invention), addition of short fibers, such as potassium titanate whiskers (the third aspect of the present invention), etc., and a solid lubricant, etc., thereby further improving

the coefficient of friction and wear resistance.

On the other hand, application of such means to the shaft sliding surface is generally difficult, except for ordinary mere spraying or coating of the resin. If the bonding force between the shaft sliding surface and the resin layer can be improved, it will be also possible to add a solid lubricant or additives such as short fibers, etc., for example, potassium titanate whiskers, etc. to the resin layer on the shaft sliding surface. Therefore a thermosetting resin having superior bonding force is preferably used for the resin on the shaft (the second aspect of the present invention).

Preferable application example of a bearing structure comprising the shaft and the bearing is an application to a continuously variable transmission (the fifth aspect of the present invention).

According to the first aspect of the present invention, a bearing structure comprises a shaft and a bearing for supporting the shaft, the shaft and the bearing having a resin layer formed on the respective sliding surfaces, where the resin layer on the shaft sliding surface is made from a resin composition comprising at least one member selected from the group consisting of epoxy resin, phenol resin, polyamideimide resin, polyimide resin, polyacetal resin, polyamide resin, polyphenylene sulfide resin, polyether ether ketone resin and tetrafluoroethylene-perfluoroalkylvinyl ether copolymer resin and 5 to 50% by weight of PTFE based on the total resin composition, and the

resin layer on the bearing sliding surface is made from at least one member selected from the group consisting of epoxy resin, phenol resin, polyamideimide resin, polyimide resin, polyacetal resin, polyamide resin, polyphenylene sulfide resin, polyether ether ketone resin and tetrafluoro-ethylene-perfluoroalkylvinyl ether copolymer resin and not more than 50% by weight of PTFE based on the total resin composition. The bearing structure can be given a lower coefficient of friction and a distinguished wear resistance thereby.

According to the second aspect of the present invention, the resin layer on the shaft sliding surface is made from a thermosetting resin, and the resin layer on the bearing sliding surface is made from a thermoplastic resin in the bearing structure according to the first aspect of the present invention. Particularly the resin layer on the shaft sliding surface in the bearing structure can be a more improved wear resistance thereby.

According to the third aspect of the present invention, the resin layer on the bearing sliding surface contains 5 to 30% by weight of potassium titanate whiskers in the bearing structure according to the first or second aspect of the present invention. The bearing structure can be given a much lower coefficient of friction and a much improved wear resistance thereby.

According to the fourth aspect of the present invention, the resin layer on the bearing sliding surface contains 0.1 to 10% by weight of a lead compound in the bearing

structure according to the first, second or third aspect of the present invention. The bearing structure can be given a much lower coefficient of friction and a much improved wear resistance thereby.

5   According to the fifth aspect of the present invention, the bearing structure according to the first, second, third or fourth aspect of the present invention is applied to the bearing structure of a continuously variable transmission. A continuously variable transmission can be

10   given a distinguished endurance thereby.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-sectional view of a continuously variable transmission.

Fig. 2 is an enlarged cross-sectional view of the

15   driving pulley region of the continuously variable transmission of Fig. 1.

DESCRIPTION OF PREFERRED EMBODIMENTS

Examples of the present invention as applied to a sliding bearing will be described below, together with

20   Comparative Examples.

At first, test pieces of bearings and shafts used in Examples 1 to 24 and Comparative Examples 1 to 11 given in Tables 1 and 2 were prepared.

Bearing test pieces were prepared in the following

25   manner:

Bronze powder was spreaded onto a 1.5 mm-thick

copper-plated steel sheet to a thickness of 0.4 mm, followed by sintering to form a porous sintered layer.

Separately, a 0.5 mm-thick resin sheet was formed from resin pellets of uniform composition given in Table 1 by a sheet extruder, and then laid onto the porous sintered layer while heating the porous sintered layer at 400° to 450°C, followed by pressure welding between rolls to conduct impregnation coating. Then, the steel sheet was cut into thrust washers, 27.2 mm in outer diameter and 22 mm in inner diameter, which were used as bearing test pieces of Examples 1 to 24 and Comparative Examples 1 to 11.

Shaft test pieces were prepared in the following manner:

Resin of the composition of one of Examples 1 to 24 and Comparative Examples 1 to 11 given in Tables 1 and 2 was sprayed onto the sliding surface of a hardened S55C steel shaft having a diameter which corresponds to the inner diameter of the thrust washer, followed by heating, thereby forming a resin layer having a thickness of 0.01 mm. In this manner, shaft test pieces of Examples 1 to 24 and Comparative Examples 1 to 11 were obtained.

Combinations of the shaft test pieces and bearing test pieces, as given in Examples 1 to 24 and Comparative Examples 1 to 11, were tested under a constant load of 10 Mpa and at a peripheral speed of 0.05 m/s for 4 hours by a Suzuki friction-wear tester to determine coefficients of friction and wear losses. The results are shown in Table 3.

Table 1

Example No.	Composition of resin layer on shaft sliding surface				Composition of resin layer on bearing sliding surface						
	PAI	EP	PFA	PTFE	PEEK	Thermo-plastic PI	PPS	PTFE	Potassium titanate whiskers	PbO	PbF₂
1	90			10	85			15			
2	80			20	85			15			
3	70			30	85			15			
4	60			40	85			15			
5	50			50	85			15			
6	90			10	100			0			
7	70			30	100			0			
8	50			50	100			0			
9	90			10	70			30			
10	70			30	70			30			
11	50			50	70			30			
12		70		30	85			15			
13			70	30	85			15			
14			50	50	85			15			
15	70			30		85		15			
16	70			30			85	15			
17	80			20	80			15	5		
18	80			20	75			15	10		
19	80			20	65			15	20		
20	80			20	55			15	30		
21	80			20	70			15	10	5	
22	80			20	74			15	10		1
23	80			20	70			15	10		5
24	80			20	65			15	10		10

Table 2

Comp. Example No.	Composition of resin layer on shaft sliding surface				Composition of resin layer on bearing sliding surface						
	PAI	EP	PFA	PTFE	PEEK	Thermo-plastic PI	PPS	PTFE	Potassium titanate whiskers	PbO	PbF$_2$
1	100			0	100			0			
2	100			0	85			15			
3	100			0	70			30			
4	100			0	65			35			
5	92			8	100			0			
6	15			85	100			0			
7	15			85	85			15			
8	No resin layer				100			0			
9	"				85			15			
10	"				70			30			
11	"				65			35			

Table 3

		Shaft wear loss (μm)	Bearing wear loss (μm)	Coefficient of friction	Simulation test (Hrs)
Example No.	1	5	7	0.10	100
	2	4	5	0.09	108
	3	4	2	0.07	110
	4	5	2	0.06	100
	5	6	2	0.06	95
	6	6	11	0.12	88
	7	6	9	0.10	93
	8	7	8	0.08	85
	9	5	6	0.07	105
	10	5	7	0.05	112
	11	6	7	0.04	92
	12	5	2	0.06	106
	13	7	2	0.05	97
	14	8	3	0.06	86
	15	4	3	0.09	109
	16	4	6	0.09	101
	17	2	4	0.07	115
	18	2	3	0.06	120
	19	2	3	0.06	118
	20	3	4	0.06	110
	21	2	2	0.05	125
	22	1	3	0.05	122
	23	1	2	0.04	127
	24	2	3	0.04	121
Comp. Example No.	1	14	23	0.31	63
	2	13	14	0.11	76
	3	11	8	0.11	70
	4	11	14	0.10	78
	5	14	16	0.18	72
	6	20	10	0.04	68
	7	19	3	0.04	70
	8	0	47	0.41	13
	9	0	19	0.16	70
	10	0	23	0.13	62
	11	0	30	0.13	50

Comparative Examples 8 to 11 with no resin layer on the shaft sliding surface each show higher coefficients of friction and larger bearing wear loss. At 15% by weight of PTFE (Comparative Example 9) or higher in the resin layer on the bearing sliding surface the coefficient of friction is not remarkably reduced. Bearing wear loss of Comparative Example 9 is minimum, whereas at 30 and 35% by weight of PTFE (Comparative Examples 10 and 11, respectively) the bearing wear loss is larger than that of Comparative Example 9 on the contrary.

Comparative Examples 1 to 4 with no PTFE in the resin layer on the shaft sliding surface each show larger wear loss on both shaft and bearing sliding surfaces. At 15% by weight of PTFE (Comparative Example 2) or higher in the resin layer on the bearing sliding surface the coefficient of friction is not remarkably reduced. Bearing wear loss is the minimum at 30% by weight of PTFE in the resin layer on the bearing sliding surface (Comparative Example 3), where it is larger at 35% by weight of PTFE (Comparative Example 4) than that of Comparative Example 3. On the other hand the shaft wear loss is 11 μm at 30% by weight of PTFE in the resin layer on the bearing sliding surface.

Examples 6 to 8 with no PTFE in the resin layer on the bearing sliding surface each show smaller coefficients of friction, and also show smaller wear losses on both shaft and bearing sliding surfaces than that of Comparative Example 1. Thus, the effect of PTFE contained in the resin layer on the shaft sliding surface is observable. The coefficient of

friction is lowered with increasing content of PTFE in the resin layer on the shaft sliding surface, but at 10% by weight of PTFE (Example 6) or higher the improvement effect of the contained PTFE is not so remarkable, as compared with

5   Comparative Example 1 containing no PTFE also in the resin layer on the shaft sliding surface. The wear loss does not change so remarkably and shows substantially the same value as 6 μm or 7 μm even against changing PTFE content from 10 to 50% by weight in the resin layer on the shaft sliding

10   surface. On the other hand, the bearing wear loss gradually decrease with increasing PTFE content in the resin layer on the bearing sliding surface. Comparative Example 6 is a case containing 85% by weight of PTFE in the resin layer on the shaft sliding surface and shows a considerably large shaft

15   wear loss such as 20 μm.

Examples 1 to 5 each contain 15% by weight of PTFE in the resin layer on the bearing sliding surface in contrast to Examples 6 to 8 and show a much lower coefficient of friction. Furthermore, both shaft and bearing wear losses

20   are smaller and the effect of PTFE contained in the resin layer on the bearing sliding surface is remarkable. The coefficient of friction gradually lowers with increasing PTFE content in the resin layer on the shaft sliding surface, whereas the shaft wear loss does not change so remarkably

25   against changing PTFE content from 10 to 50% by weight in the resin layer on the shaft sliding surface, where the shaft wear loss of Examples 2 and 3 are 4 μm as a minimum. On the other hand, the bearing wear loss of Examples 3, 4 and 5 is

2 μm as a minimum. Comparative Example 7 is a case containing 85% by weight of PTFE in the resin layer on the shaft sliding surface and shows a considerably large shaft wear loss such as 19 μm.

5   Examples 9 to 11 each contain 30% by weight of PTFE in the resin layer on the bearing sliding surface in contrast to Examples 6 to 8 and show most distinguished coefficients of friction. The shaft wear loss does not change remarkably against changing PTFE content from 10 to 50% by weight in 10 the resin layer on the shaft sliding surface and shows small values such as 5 μm and 6 μm. The bearing wear loss also shows small values such as 6 μm and 7 μm.

      It can be seen from the foregoing test results that a coefficient of friction can be made smaller and the shaft 15 and bearing wear resistances can be improved by making the resin layer on the shaft sliding surface from a resin composition comprising PAI (polyamideimide resin) and at least 5% by weight of PTFE on the basis of the total resin composition and making the resin layer on the bearing sliding 20 surface from a resin composition comprising PEEK (polyether ether ketone resin) and not more than 30% by weight of PTFE on the basis of total resin composition.

      Examples 12 and 13 are cases of using EP (epoxy resin) and PFA (tetrafluoroethylene-perfluoroalkylvinyl 25 ether copolymer resin), respectively, for the resin layer on the shaft sliding surface in place of PAI of Example 3, and each show equivalent values for the coefficient of friction and the shaft and bearing wear losses.

Examples 15 and 16 are cases of using thermoplastic PI (polyimide resin) and PPS (polyphenylene sulfide resin), respectively, for the resin layer on the bearing sliding surface in place of PEEK of Example 3, and each show equivalent

5 values for the coefficient of friction and the shaft and bearing wear losses.

Examples 17 to 20 are cases of adding 5 to 30% by weight of potassium titanate whiskers to the resin layer on the bearing sliding surface on the basis of the total resin

10 composition, while keeping the PTFE content of 15% by weight constant in contrast to the resin layer comprising 85% by weight of PEEK and 15% by weight of PTFE on the bearing sliding surface of Example 2, and each show much better values for the coefficient of friction and the shaft and bearing wear

15 losses.

Examples 21 to 24 are cases of adding PbO or PbF_2 to the resin layer on the bearing sliding surface on the basis of the total resin composition, while keeping the PTFE content of 15% by weight constant, in contrast to the resin

20 layer on the bearing sliding surface of Example 18, and each show much better values for the coefficient of friction and the shaft and bearing wear losses.

Example

(Application to a continuously variable

25 transmission)

An embodiment of applying the present invention to a dry type, continuously variable transmission will be

described below:

Fig. 1 is a cross-sectional view of a belt-type, continuously variable transmission, where driving shaft 2 connected to an engine (not shown in the drawing) and driven shaft 3 connected to a wheel (not shown in the drawing) are rotatably mounted on casing 1, and driving pulley 20 is formed on driving shaft 2 whereas driven pulley 30 is formed on driven shaft 3. V belt 4 is entrained between pulley grooves on both pulleys 20 and 30. When driving shaft 2 is driven to rotate, driven shaft 3 is rotated in a transmission ratio corresponding to respective diameters of V belt 4 entrained pulleys 20 and 30.

Driving pulley 20 will be further explained below.

At the intermediate position of driving shaft 2 rotatably mounted on casing 1 is integrally provided fixed sheave 21, which can serve as a half of driving pulley 20. Slide key 22 is provided on driving shaft 2 as projected from the other periphery of the shaft body and cylindrical driving housing 23 is provided sliding in the axial direction, while fitted with slide key 22. Driving housing 23 is also rotatable together with driving shaft 2. On the inner periphery of driving housing 23 are provided bearings 24 at two positions around driving shaft 2 to support driving housing 23.

The outer periphery of driving housing 23 is fitted with the inner race ring of bearing 51 to allow driving housing 23 to rotate together with the inner race ring. On the other hand, the outer race ring of bearing 51 is fitted with slider

gear 52 to allow the outer race ring to rotate together with slider gear 52.

Internal threads 52a are formed on the inner peripheral surface of slider gear 52 and are engaged with external threads 53a formed on screw shaft 53. The end of screw shaft 53 is fixed to casing 6, and bearing 54 is provided on the inside of screw shaft 53, and driving shaft 2 is rotatably supported on bearing 54.

Gear 52b is formed on the outer periphery of slider gear 52 and is engaged with small gear 55a on rotatably supported power transmission gear 55. On the other hand, large gear 55b on power transmission gear 55 is engaged with small gear 56a on power transmission gear 56, and large gear 56b on power transmission gear 56 is engaged with driving gear 57 on motor 5. Driving gear 57 is driven by motor 5. Rotation of motor 5 is transmitted to slider gear 52 through power transmission gears 56 and 55. Slider gear 52, when rotated, slides in the axial direction by threads 52a and 53a.

Thus, driving housing 23 is slidable in the axial direction of driving shaft 2 by rotation of motor 5. Movable sheave 25 serving as another half of driving pulley 20 is integrally provided on driving housing 23 at one end thereof. A V-shaped driving pulley groove is formed between the counterposed inclined surfaces of movable sheave 25 and fixed sheave 21. When motor 5 is started to rotate, driving housing 23 slides in the axial direction of driving shaft 2, whereby

movable sheave 25 is slided to adjust the width of driving pulley groove.

Groove width-adjustable, V-shaped driving pulley groove can be provided in this manner by fixed sheave 21 on driving shaft 2 and movable sheeve 25 on driving housing 23. V belt 4 is then entrained between the V-shaped driving pulley groove and the driven pulley groove of driven pulley 30.

Driven pulley 30 will be further explained below.

Driven pulley 30 is substantially in the same structure as that of driving pulley 20. On driven shaft 3 mounted on casing 1 in parallel with driving shaft 2 is integrally provided fixed sheave 31 serving as a half of driven pulley 30 at the position corresponding to that of movable sheave 25 on driving pulley 20. Cylindrical driven housing 32, which is slidable in the axial direction of driven shaft 3, is provided on driven shaft 3, and is rotatable together driven shaft 3.

On the inner peripheral surface of driven housing 32 are provided bearings 33 at two positions around driven shaft 3 to support driven housing 32 and also to allow driven housing 32 to rotate with driven shaft 3 and slide in the axial direction of driven shaft 3.

Movable sheave 36 serving as another half of driven pulley 30 is integrally provided on driven housing 32 at one end, and a driven pulley groove is formed between the inclined surfaces of counterposed movable sheave 36 and fixed sheave 31. In Fig. 1, the right end surface of movable sheave 36 forms a torque-cam surface, and torque-cam 34, which can be

engaged with the torque-cam surface, is provided on driven shaft 3. Driven housing 32 is pressed toward the left by a compression spring 35 inserted therebetween and the torque-cam mechanism, thereby generating a tension on V belt

5 4.

Movable sheave 25 on driving shaft 2 can be slided toward the left or the right in this manner, thereby broadening or narrowing the width of the driving pulley groove, and correspondingly the width of the driven pulley

10 groove can be changed, i.e. broadened or narrowed by V belt 4 entrained therebetween, thereby changing the respective pulley diameter. That is, continuously variable transmission can be established between driving shaft 2 and driven shaft 3 thereby.

15   Bearings 24 provided on driving housing 23 will be further explained below.

Driving housing 23 rotates together with driving shaft 2 by engagement of slide key 22, but a very small clearance is provided between bearings 24 and driving shaft

20 2 to allow driving housing 23 to smoothly slide in the axial direction along driving shaft 2. The inner peripheral length of cylindrical bearings 24 is larger only by a length corresponding to the clearance than the outer peripheral length of driving shaft 2. On the other hand, driving housing

25 23 and driving shaft 2 rotate together by V belt 4, and thus bearings 24 produce a scroll motion on driving shaft 2. As a result, wear generates on the sliding surfaces of bearings

24 and driving shaft 2 due to frictions caused by the scroll motion.

To allow driving housing 23 to smoothly slide in the axial direction in the bearing structure of driving shaft 2 and bearings 24, it is required that the coefficient of friction is low and stable, wear losses of both driving shaft 2 and bearings 24 are small and the clearance is kept within an appropriate range.

As shown by arrow in Fig. 2, driving housing 23 is subject to a tilting force due to the tension on V belt 4, and consequently tends to slide on driving shaft 2 in a partial or one-side contact with bearings 24.

Bearings 33 provided on driven housing 32, which rotates together with driven shaft 3, produce a scroll motion on driven shaft 3 due to a difference in inner peripheral length caused by the clearance as in case of bearings 24 on driving housing 23. Consequently, wear generates on the sliding surfaces of bearings 33 and driven shaft 3 due to frictions caused by the scroll motion. That is, driven housing 32 tend to slide on driven shaft 3 in a partial or one-side contact with bearings 33 due to the tension on V belt 4, as in case of the bearing structure of driving shaft 2 and bearings 24.

The bearing structure of driving shaft 2 and bearings 24 and that of driven shaft 3 and bearings 33 were tested to determine their wear resistances. Test was carried out by a pulley bearing wear tester for a continuously variable transmission disclosed in JP-A 9(1997)-113429.

The wear tester is a simulation tester capable of providing the same sliding conditions as these for actual transmissions. Test conditions were set as follows:

Revolution of driving shaft 2: 3,200 rpm

Revolution of driven shaft 3:   6,400 rpm

Interaxial force: 500 kgf

Clearances between shaft and bearing: 100 μm each wear loss was measured at an interval of 10 hours, and the time when the clearance reached 200 μm by wearing of the shafts and the bearing on the basis of the measurements, was regarded as endurance time, by which the wear resistance was judged. However, since wear loss was larger on the driven shaft than on the driving shaft, wear loss on the driven shaft was used as endurance time

Test pieces were those consisting of shafts or bearings and resin layer of Examples 1 to 24 and Comparative Examples 1 to 11 given in Tables 1 and 2. That is, bearing test pieces were prepared, as in the same manner as mentioned before, by roll pressure-welding the resin composition onto a porous sintered layer, followed by cutting, formation of cylinders, 36 mm in inner diameter and 25 mm in width, and further cutting of inner surface by a general purpose lathe to enhance the dimensional precision. In this manner, bearing test pieces of Examples 1 to 24 and Comparative Examples 1 to 11 were obtained.

Shaft test pieces were prepared by spraying resin compositions of Examples 1 to 24 and Comparative Examples 1 to 7 in a band state, 40 mm in width, onto the outer periphery

of a steel shaft, 36 mm in diamter, followed by heating to form a resin layer, 0.01 mm in thickness. Shaft test pieces of Examples 1 to 24 and Comparative Examples 1 to 7 were obtained thereby.

5   Results of endurance time on the driven shaft side obtained by the simulation test are shown in Table 3.

    The test results show that good endurance was obtained in all the Examples, as compared with Comparative Examples 8 to 11 with no resin layer on the shaft sliding

10 surface, and also as compared with Comparative Examples 1 to 4 with no PTFE in the resin layer on the shaft sliding surface.

WHAT IS CLAIMED IS:

1.   A bearing structure, which comprises a shaft and a bearing for supporting the shaft, the shaft and the bearing having a resin layer formed on the respective sliding surfaces, the resin layer on the shaft sliding surface being made from a resin composition comprising at least one member selected from the group consisting of epoxy resin, phenol resin, polyamideimide resin, polyimide resin, polyacetal resin, polyamide resin, polyphenylene sulfide resin, polyether ether ketone resin and tetrafluoroethylene-perfluoroalkylvinyl ether copolymer resin and 5 to 50% by weight of polytetrafluoroethylene based on total resin composition, and the resin layer on the bearing sliding surface being made from at least one member selected from the group consisting of epoxy resin, phenol resin, polyamideimide resin, polyimide resin, polyacetal resin, polyamide resin, polyphenylene sulfide resin, polyether ether ketone resin, tetrafluoroethylene-perfluoro-alkylvinyl ether copolymer resin and not more than 50% by weight of polytetrafluoroethylene based on total resin composition.

2.   A bearing structure according to Claim 1, wherein the resin layer on the shaft sliding surface is made from a thermosetting resin and the resin layer on the bearing sliding surface is made from a thermoplastic resin.

3.   A bearing structure according to Claim 1 or 2, wherein the resin layer on the bearing sliding surface contains 5 to 30% by weight of potassium titanate whiskers

based on total resin composition.

4.   A bearing structure according to Claim 1, 2 or 3,
wherein the resin layer on the bearing sliding surface
contains 0.1 to 10% by weight of a lead compound, based on
total resin composition.

5.   A continuously variable transmission having a
bearing structure according to Claim 1, 2, 3 or 4.

6.   A bearing structure substantially as hereinbefore
described with reference to and as shown in the accompanying drawings.

7.   A continuously variable transmission substantially
as hereinbefore described with reference to and as shown in the
accompanying drawings.

<u>Translation of the Office Action dated January 23, 2007</u>

<u>issued by the German Patent and Trademark Office,</u>

<u>regarding the German Patent Application No. 103 40 427.9</u>

Request for examination, date of payment: September 02, 2003.

In response to the submission of May 11, 2005, received on the same day.

The further examination of the above-mentioned Patent Application has led to the result as set forth below.

For filing a response, a term of **four months** has been granted. The term starts to run at the day following the receipt of the Office Action.

Notice Regarding the Possibility of Branching off a Utility Model

The Applicant of a patent application filed with effect in the Federal Republic of Germany can file a utility model application relating to the same application and simultaneously claim the application date of the prior patent application. This branching off (§ 5 Utility Model Act) is possible until the expiration of two months after the end of that month in which the patent application has been settled by legal rejection, withdrawal at the applicant's own free will or fictitious withdrawal, an opposition procedure has been concluded, or - in the case of the grant of the patent - the time limit for lodging an appeal against the decision to grant a patent has lapsed without an appeal having been filed. More detailed information in connection with the requirements for a utility model application, including the branching off, are contained in the Information Sheet for the filing of utility model applications (G 6181) which can be obtained free of charge at the Patent and Trademark Office and the Patent Information Centres.

Claims 1 to 21, which have been filed with the above-mentioned submission, will be taken as a basis for the further examination procedure, which according to the original disclosure (cf. originally filed claims 1 to 18) are not to be objected.

As a further state of the art, following documents have been ascertained, which are herewith newly-introduced into the procedure:

(8)   DE 697 09 141 T2
(9)   DE 199 46 193 A1
(10)   JP 2000169738 A including an English machine-translation
(11)   RÖMPP Online: " Polytetrafluorethylene", [online]. Version 2.12 Georg Thieme Verlag, 2007.
(12)   Ullmann's Encyclopedia of Industrial Chemistry: "Fluropolymers, Organic", [online]. 6. ed. Weinheim, Wiley-VCH, 2005. DOI: 10.1002/14356007.a11_393.

On the basis of the present application documents, prospects for the grant of a patent can still not be held out.

A resin composition according to claim 1 was already known from state of the art prior to the priority date (cf. document (8), claims 1 and 2 as well as description pages 4/5 (polyether ether ketone as resin), page 6, penultimate paragraph and page 9, last paragraph).

Thus, the claimed resin composition lacks novelty, which is mandatory for the grant of a patent. Claim 1 is therefore not allowable.

Moreover, the composition according to claim 1 does not involve an inventive step either.

Document (9) discloses a sliding resin composition, in which the thermosetting resin constitutes the base resin, and PTFE (up to 50 wt.-%) as well as a lead compound (0.1-10 wt.-%) are contained.

In documents (4) and (5) (already indicated in the application), PTFE containing lubricants are mentioned, in which lead is not used as an additive because of environmental protection reasons, and thus, it is displaced by bismuth, bismuth alloys or BaSo$_4$ (cf. document (4), claim 1 and description pages 1/2, bridging paragraph, as well as page 2, lines 6-11; cf. document (5), Abstract).

From citation (4), a person skilled in the art gains suggestion to replace environmentally unfriendly lead — also used in the composition according to document (9) (compounds of base resin, PTFE and lead) — by bismuth and/or bismuth alloys. Knowing the teaching of state of the art, it was to be expected that by implementation of this measure, a sliding composition with the desired requirements can be achieved. An inventive step can thus not be sustained.

Claim 1 is therefore not allowable as to lack of inventive step.

The above objection regarding the main claim applies equally to independent claims 2 and 3. Therefore, they cannot be considered as involving an inventive step, either. Herein, besides document (4), documents (5) and (6) (use of BaSO$_4$) are additionally to be considered in the discussion (as to dependent claim 2, cf. Abstract of document (5); as to dependent claim 3, cf. document (6), claims 1 to 3 and description, column 2, lines 4-7).

Regarding claim 2, it is also referred to document (10), which discloses a composition of thermosetting resin (polyether ketone, polyimide), PTFE ("Teflon 6J" analogue application) and an alkaline earth metal phosphate. For this reason, the subject-matter of claim 2 lacks novelty vis-à-vis document (10) and is, therefore, not allowable.

As to the molecular weight of PTFE, it is annotated that the standard molecular weights for PTFE are in the range between $5*10^6$ and 10^7 g/mol (cf. as general reference documents (11) and (12)). Documents cited during the procedure do not contain any hint that PTFE, which is used as a lubricant, has molecular weights smaller than 600,000 g/mol. On the contrary, document (10) would suggest to a person skilled in the art to use PTFE with molecular weights > 3 000 000 g/mol

("Teflon 6J"). An expert considering document (9) will thus use a standard, commercially available PTFE, which will at any rate contain amounts of PTFE with molecular weights greater than 3 000 000 g/mol, or he will immediately use "Teflon 6J" described in document (10).

Incidentally, in claim 1 it is not disclosed whether the number-average molecular weight of molecular weight M_n is concerned, or the weight-average molecular weight of molecular weight M_w. Thus, claim 1 is unclear and alone for that reason unallowable.

Subclaims 4 and 9 will fall as being referred back to the also non-allowable claims 1 and 3.

Method claims are neither allowable as to lack of inventive step (cf. document (9) in combination with documents (4), (5) or (6)).

A patent cannot be granted on the basis of the application documents currently on file; rather rejection of the application must be expected.

Should a statement in this matter not be intended, an informal notification about the receipt of this Official Action is requested.

Examiner in charge of Class **C 08 L**
Dr. Kammermeier

<u>Encl:</u>
Copies of 5 references

4

Deutsches Patent- und Markenamt

München, den 23.01.2007

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EINGEGANGEN

0 5. Feb. 2007

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Patent- und Rechtsanwälte
Kraus & Weisert
Thomas-Wimmer-Ring 15
80539 München

Prüfungsantrag, Einzahlungstag am 02.09.2003

Eingabe vom 11.05.2005   **eingegangen am 11.05.2005**

Die weitere Prüfung der oben genannten Patentanmeldung hat zu dem nachstehenden Ergebnis geführt.

Zur Äußerung wird eine **Frist von**

4 Monat(en)

gewährt. Die Frist beginnt an dem Tag zu laufen, der auf den Tag des Zugangs des Bescheids folgt.

Für Unterlagen, die der Äußerung gegebenenfalls beigefügt werden (z. B. Beschreibung, Beschreibungsteile, Patentansprüche, Zeichnungen), sind je **zwei** Ausfertigungen auf gesonderten Blättern erforderlich. Die Äußerung selbst wird nur in einfacher Ausfertigung benötigt.

Werden die Beschreibung, die Patentansprüche oder die Zeichnungen im Laufe des Verfahrens geändert, so hat der Anmelder, sofern die Änderungen nicht vom Deutschen Patent- und Markenamt vorgeschlagen sind, im Einzelnen anzugeben, an welcher Stelle die in den neuen Unterlagen beschriebenen Erfindungsmerkmale in den ursprünglichen Unterlagen offenbart sind.

☐ Werden die vom Deutschen Patent- und Markenamt vorgeschlagenen Änderungen ohne weitere Änderung vom Anmelder angenommen, ist den Reinschriften eine Erklärung beizufügen, dass die Reinschriften keine über die vom Deutschen Patent- und Markenamt vorgeschlagenen Änderungen hinausgehende Änderungen enthalten (§ 15 Absatz 4 PatV).

☐ In diesem Bescheid ist/sind folgende Entgegenhaltung/en erstmalig genannt. (Bei deren Nummerierung gilt diese auch für das weitere Verfahren):

Hinweis auf die Möglichkeit der Gebrauchsmusterabzweigung

Der Anmelder einer mit Wirkung für die Bundesrepublik Deutschland eingereichten Patentanmeldung kann eine Gebrauchsmusteranmeldung, die den gleichen Gegenstand betrifft, einreichen und gleichzeitig den Anmeldetag der früheren Patentanmeldung in Anspruch nehmen. Diese Abzweigung (§ 5 Gebrauchsmustergesetz) ist bis zum Ablauf von 2 Monaten nach dem Ende des Monats möglich, in dem die Patentanmeldung durch rechtskräftige Zurückweisung, freiwillige Rücknahme oder Rücknahmefiktion erledigt, ein Einspruchsverfahren abgeschlossen oder - im Falle der Erteilung des Patents - die Frist für die Beschwerde gegen den Erteilungsbeschluss fruchtlos verstrichen ist. Ausführliche Informationen über die Erfordernisse einer Gebrauchsmusteranmeldung, einschließlich der Abzweigung, enthält das Merkblatt für Gebrauchsmusteranmelder (G 6181), welches kostenlos beim Patent- und Markenamt und den Patentinformationszentren erhältlich ist.

Dem weiteren Prüfungsverfahren werden die mit o.g. Eingabe eingereichten Patentansprüche 1 bis 21 zugrunde gelegt, die hinsichtlich der ursprünglichen Offenbarung (vgl. ursprünglich eingereichte Ansprüche 1 bis 18) nicht zu beanstanden sind.

Als weiterer Stand der Technik wurden folgende Druckschriften ermittelt, die hiermit neu in das Verfahren eingeführt werden:

(8) DE 697 09 141 T2
(9) DE 199 46 193 A1A
(10) JP 2000169738 A sowie englische Maschinenübersetzung
(11) RÖMPP Online: „Polytetrafluorethylene", [online]. Version 2.12 Georg Thieme Verlag, 2007.
(12) Ullmann's Encyclopedia of Industrial Chemistry: „Fluropolymers, Organic",
   [online]. 6. Aufl. Weinheim, Wiley-VCH, 2005. DOI: 10.1002/14356007.a11_393.

Die Erteilung eines Patentes auf den vorliegenden Anmeldungsgegenstand kann auch weiterhin nicht in Aussicht gestellt werden.

Eine Harzzusammensetzung gemäß Anspruch 1 war bereits vor dem Prioritätstag aus dem Stand der Technik bekannt gewesen (vgl. (8), Ansprüche 1 und 2 sowie Beschreibung Seiten 4/5 (Polyetheretherketon als Harz), Seite 6 vorletzter Absatz + Seite 9 letzter Absatz). .

Die beanspruchte Harzzusammensetzung besitzt deshalb nicht die zur Erteilung eines Patentes erforderliche Neuheit. Anspruch 1 ist deshalb nicht gewährbar.

Daneben beruht die Zusammensetzung gemäß Anspruch 1 auch nicht auf der nötigen erfinderischen Tätigkeit.

Entgegenhaltung (9) beschreibt eine gleitend machende Harzzusammensetzung, in der das wärmehärtbare Harz das Basisharz darstellt und PTFE (bis 50 Gew.-%) und eine Bleiverbindung (0.1 -10 Gew-%) enthalten sind.

In den Entgegenhaltungen (4) und (5) (in der Anmeldung erwähnt) werden PTFE enthaltende Gleitmittel genannt, in denen aus Umweltschutzgründen auf Blei als Zusatzmittel verzichtet wird und das Blei durch Bismut, Bismutlegierungen oder $BaSO_4$ ersetzt wird (vgl. (4) An-

Mit den Ansprüchen 1 bis 3 fallen auch die darauf aufbauenden Unteransprüche 4 bis 9.

Die Verfahrensansprüche sind mangels erfinderischer Tätigkeit ebenfalls nicht gewährbar (vgl. (9) in Kombination mit (4), (5) oder (6)).

Mit den vorliegenden Unterlagen kann eine Patenterteilung nicht erfolgen; es muss vielmehr mit der Zurückweisung der Anmeldung gerechnet werden.

Falls eine Äußerung in der Sache nicht beabsichtigt ist, wird eine formlose Mitteilung über den Erhalt des Bescheides erbeten.

Prüfungsstelle für Klasse C08L

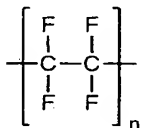Dr. Kammermeier
(Hausruf 3884)

Anlage
Abl. von 5 Druckschriften

RÖMPP Online, Version 2.12

Polytetrafluorethylene

Fachgebiet Chemie, Unterthema Makromolekulare Chemie

(Kurzz. PTFE). Bez. für Polymere des Tetrafluorethylens mit der allg. Formel:

Techn. Produkte haben Polymerisationsgrade von ca. 5000 –100000, was Molmassen von ca. 500000 –10000000 g/mol entspricht.

Die Polymerisation der Monomeren wird radikal. initiiert u. unter Druck mittels Emulsions- od. Suspensionspolymerisation durchgeführt, um die hohe Polymerisationswärme abzuführen. Bei der Polymerisation in Suspension wird das P. als Granulat erhalten, das zur gewünschten Partikelgröße vermahlen wird. Feinpulvrige P.-Produkte werden dagegen nur durch Emulsionspolymerisation erhalten. Unter geeigneten Bedingungen sind beim Einsatz ion. Tenside als Stabilisatoren auch feinteilige stabile Dispersionen mit Feststoff-Gehalten von 60 –65% herstellbar.

Eigenschaften:

P. sind thermoelast. Polymere mit hoher Linearität, relativ hohem (bis 70%) Kristallinitätsgrad u. einem Schmp. von ca. 327°C, bei dem sie glasartig transparent werden. Beim Erwärmen von 20° C bis zum Schmp. tritt eine reversible Vol.-Zunahme der P. von ca. 27% auf. P. besitzen eine äußerst hohe Chemikalienbeständigkeit u. sind in allen Lsm. unterhalb 300°C unlöslich. Halogenkohlenwasserstoffe wirken quellend. P. können in einem sehr breiten Temp.-Bereich (–200°C bis 250°C) eingesetzt werden; sie besitzen hohe therm. Beständigkeit (max. Dauergebrauchs-Temp.: ca. 260°C). Bei Temp. oberhalb 400°C tritt Zers. auf; die Fluor-haltigen Zers.-Produkte, u.a. Fluorphosgen (COF_2) od. Perfluorisobuten, sind äußerst toxisch. Sie können beim Menschen bei längerer Einwirkung zu grippeähnlichen Erkrankungen (*Polymerdampf-Fieber*) u. zu Lungenödemen führen.

P. besitzen nur sehr geringes Adhäsionsvermögen; zum Verkleben müssen P.-Teile oberflächlich aktiviert werden (CASING-Verfahren). P. zeigen sehr gute (di)elektr. Eigenschaften, sind physiolog. unbedenklich u. nicht brennbar.

Für bes. anspruchsvolle Anw., bei denen z.B. hohe Kriechfestigkeit u. niedriges Kaltfließen gefordert werden, werden P. durch Beimischen von Glasfasern, Kohlefasern, Ruß, Molybdänsulfid od. Polymeren wie Polyimide, Polyetherketone, od. Polyphenylensulfide verstärkt.

Eigenschaftsveränderungen der P. sind auch über Copolymerisationen des Basis-Monomeren mit anderen (Fluor-haltigen) Comonomeren (s. Monomere) möglich (Tetrafluorethylen-Copolymere, s. Fluorkohlenwasserstoffe).

P. werden durch Preßsintern, Schlagpressen, Extrudieren u. Spanen verarbeitet; Kleben u. Schweißen sind möglich. Aus Dispersionen können P. auch auf Glasfasergeweben u. Metalloberflächen gesintert werden.

Verwendung:

P. kommt in Form von Folien, Platten, Stäben, Fasern (*Fluorfasern*), Röhren, Bändern usw. in den Handel. Die wichtigsten Anw.-Gebiete sind Beschichtungen u. Auskleidungen im chem. Apparatebau, Laborgeräte u. -Ausstattungen, wartungsfreie Lager u. Dichtungen, als antiadhäsive Überzüge in der Papier-, Textil-, Nahrungsmittel- u. Kunststoffverarbeitung, in der Elektro- u. Raumfahrt-Ind. u. im Flugzeugbau. Der P.-Verbrauch erreichte 1994 weltweit ein Vol. von ca. 43000 t [1].

Übersetzungen:	CAS-RN:	HS-Code:
E polytetrafluorethylene	9002-84-0	3904 61
F polytétrafluoroéthylène		
I politetrafluoroetilene		
S politetrafluoroetileno		

Literatur:

[1] Kunststoffe 85, 1590 (1995).
Batzer 3, 157f.
Domininghaus (5.), S. 525ff.
Encycl. Polym. Sci. Eng. 16, 577 –600.

Fluoropolymers, Organic

Fluorine Compounds, Organic is a separate keyword

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Abbreviations used in this article:

CTFE   chlorotrifluoroethylene
ECTFE   ethylene–chlorotrifluoroethylene copolymer
ETFE   ethylene–tetrafluoroethylene copolymer
FEP   fluorinated ethylene–propylene

	copolymer
HFP	hexafluoropropene
HFPI	hexafluoropropene index
LOI	limiting oxygen index
MI	melt-flow index
P	propene
PCTFE	polychlorotrifluoroethylene
PFA	perfluoroalkoxy copolymer
PMVE	perfluoro(methyl vinyl ether)
PPVE	perfluoro(propyl vinyl ether)
PTFE	polytetrafluoroethylene
PVC	poly(vinyl chloride)
PVDF	poly(vinylidene fluoride)
PVF	poly(vinyl fluoride)
SSG	standard specific gravity
TFE	tetrafluoroethylene
VDF	vinylidene fluoride
VF	vinyl fluoride

1. Introduction

History. The fluoropolymer industry owes its start to a fortunate accident in Du Pont's Jackson Laboratory in 1938. ROY PLUNKETT was attempting to prepare new refrigerant gases from tetrafluoroethylene (TFE). However, one morning, when the valve to the almost full TFE cylinder was opened, no gas came out. After being satisfied that the valve had not malfunctioned, he had the cylinder cut open. What he found was the first sample of polytetrafluoroethylene (PTFE), a remarkable polymer, which has become an essential material in the world today. Initially, no applications were known for this new material. However, the Manhattan Project of World War II required a material sufficiently resistant to the highly corrosive substance UF_6, an intermediate in the production of ^{235}U-enriched uranium. Polytetrafluoroethylene appeared to fill this need, spurring the development of processing and production methods for the new fluoroplastic. In 1946, PTFE was introduced commercially under the tradename Teflon. This new plastic, with its outstanding chemical, electrical, and surface properties, gained immediate acceptance in the marketplace. Since then, other fluoropolymers have been discovered and commercialized. These products include fluoroplastics and fluoroelastomers and serve an ever-expanding market, providing materials with the unique combination of properties which fluoropolymers alone can provide.

Monomers. Only four fluoroolefins have been polymerized to high molecular mass homopolymers of commercial importance. These monomers are tetrafluoroethylene (TFE), vinyl fluoride (VF), vinylidene fluoride (VDF or VF_2), and chlorotrifluoroethylene (CTFE). However, other monomers have been copolymerized with these fluoroolefins. Such copolymers have created a diversity of commercially available fluoropolymers, including both plastics and elastomers. The principal monomers from which most commercial fluoropolymers are made are listed in Table 1. The fluoromonomers are described in detail elsewhere in this volume ($\rightarrow$ Fluorine Compounds, Organic). Several other monomers are used in small amounts as modifiers and to provide cure sites.

Polymers. Among the fluoroplastics (semicrystalline polymers with $mp > 150\,°C$), several forms of PTFE and a variety of TFE copolymers are commercially available. Others are based on VF, VDF, and CTFE. In the case of fluoroelastomers (amorphous polymers with $T_g < 0\,°C$), VDF−HFP (hexafluoropropylene) copolymers and VDF−HFP−TFE terpolymers constitute the bulk of today's commercial products. Other important fluoroelastomers include TFE copolymers with propene (TFE−P), and perfluoro(methyl vinyl ether), (TFE−PMVE), fluorosilicones, and fluorophosphazenes. A special group of TFE copolymers that contain sulfonic acid and carboxylic acid functions are commercially available in the form of ion-exchange membranes ($\rightarrow$ Fluorine Compounds, Organic, Chap. 8.2.).

Production. The principal method for synthesizing organic fluoropolymers is free-radical polymerization. Because of the electrophilic nature of fluoroolefins, cationic polymerization catalysts are not effective. Fluoroolefins and epoxides can be polymerized by anionic catalysts, but termination by fluoride ion elimination prevents high molecular masses from being attained. Coordination catalysts do not effect polymerization of fluoroolefins.

The polymerization and processing techniques described in this article are described in

Table 1. Monomers used in commercial fluoropolymers

Compound	CAS registry number	Formula	Abbreviation
Ethylene	[74-85-1]	$CH_2=CH_2$	E
Tetrafluoroethylene	[116-14-3]	$CF_2=CF_2$	TFE
Chlorotrifluoroethylene	[79-38-9]	$CF_2=CClF$	CTFE
Vinylidene fluoride	[79-38-7]	$CF_2=CH_2$	VDF (VF$_2$)
Vinyl fluoride	[75-02-5]	$CFH=CH_2$	VF
Propene	[115-07-1]	$CH_3CH=CH_2$	P
Hexafluoropropene	[116-15-4]	$CF_3CF=CF_2$	HFP
Perfluoro(methyl vinyl ether)	[1187-93-5]	$CF_3OCF=CF_2$	PMVE
Perfluoro(propyl vinyl ether)	[1623-05-8]	$CF_3CF_2CF_2OCF=CF_2$	PPVE

detail elsewhere (→Polymerization Processes, → Plastics, Processing).

Properties. The properties of fluoropolymers vary with the fluorine content and with the distribution of fluorine atoms in the molecule. The carbon–fluorine bond is one of the strongest organic bonds. Substitution of fluorine for hydrogen in a hydrocarbon polymer generally increases chemical and oxidative stability, weatherability, and melting point. The presence of fluorine reduces flammability, solubility in hydrocarbons, adhesiveness, radiation resistance, and the coefficient of friction. Each fluoropolymer has its own unique combination of properties. Cost generally increases with fluorine content.

Uses. Numerous uses have been found for fluoropolymers, many of which cannot be satisfied by any other material.

Fluoroplastics find their greatest utility in electrical applications such as insulation, flexible printed circuits, and piezoelectric devices. Other applications include chemically resistant coatings, bearings, nonstick surfaces, architectural fabric (dome construction), laboratory ware, heat exchangers, heart valves and other prosthetic devices, and water-repellent fabric.

Fluoroelastomers have found their greatest use in sealing applications, such as O-rings, gaskets, valve stem seals, and shaft seals. They are also used in flue duct expansion joints, as linings for fuel hoses, binders for military flares, and processing aids for polyethylene film extrusion.

2. Fluoroplastics

2.1. Introduction

The family of thermoplastic fluoropolymers is headed by polytetrafluoroethylene (PTFE). Other members include TFE–HFP copolymers (FEP), TFE–PPVE copolymers (PFA), and TFE–ethylene copolymers (ETFE), as well as polychlorotrifluoroethylene (PCTFE) and CTFE–ethylene copolymers (ECTFE). Poly(vinyl fluoride) (PVF), poly(vinylidene fluoride) (PVDF), and copolymers of VDF are also important.

Since the high melt viscosity of PTFE resins prevents processing by conventional extrusion and molding techniques, they are processed by sintering techniques similar to those used in powder metallurgy. Although PTFE can be converted into practically any form (rods, billets, films, fibers, tubing, or coatings) by these techniques, the lack of melt processibility is frequently a handicap. Research on melt-processible forms of PTFE began almost immediately after its discovery [5]. The first to be developed was a TFE–HFP copolymer called FEP (fluorinated ethylene–propene) copolymer [6]. The FEP resins, commercialized in 1960, share nearly all the properties of PTFE, but are also processible by extrusion and injection molding. However, the melting point of FEP is ca. 60–70 °C lower than that of PTFE; its maximum use temperature is also lower. Further research on TFE copolymers led to the development of perfluoroalkoxy (PFA) resins, which are TFE–PPVE copolymers [7] that were introduced commercially in 1972. These have the same high-temperature properties as PTFE resins and an even lower melt viscosity than

FEP resins; they can be processed by extrusion and injection molding. In 1970 ETFE resins (TFE—ethylene copolymers) were commercialized [8]. They exhibit improved mechanical properties and far better processibility than other TFE copolymers. In addition, they can be crosslinked by high-energy radiation. The maximum use temperature, however, is lower than that of PFA or FEP.

Among the fluoroplastics that contain monomers other than TFE, PCTFE was the first to be commercialized. Extensive development work was carried out on this polymer during World War II in conjunction with the Manhattan Project [9]. Compared to TFE resins, PCTFE is harder, more resistant to creep, and less permeable. It has the lowest permeability to moisture of any plastic. Chlorotrifluoroethylene copolymerized with VDF provides an improved resin for film manufacture. However, ECTFE is the most important CTFE copolymer [10]. These resins are similar in properties and uses to ETFE copolymers.

Poly(vinyl fluoride) (PVF) contains the smallest amount of fluorine (41.3 %) of any commercial fluoropolymer, but possesses many of the properties of more highly fluorinated polymers [11]. It was commercialized in 1961 by Du Pont under the trade name Tedlar. It is used mainly in coatings for metal, plastic, paper, and similar substrates to provide resistance to weather, chemicals, staining, and abrasion.

Poly(vinylidene fluoride) (PVDF) shares many of the characteristics of other fluoropolymers such as thermal and oxidative stability, as well as outstanding weatherability [12]. However, the arrangement of alternate fluorine and hydrogen atoms leads to unusual polarity within the polymer chains, with a dramatic effect on dielectric properties and solubility. An unusual product made from PVDF is a film with piezoelectric properties. Copolymerization of VDF with a small amount (< 15 %) of HFP reduces stiffness and improves processibility for certain wire coating applications.

2.2. Polytetrafluoroethylene

Polytetrafluoroethylene [9002-84-0] (PTFE) is a straight-chain polymer of tetrafluoroethylene (TFE) of the general formula

$$-(CF_2CF_2-)_n-$$
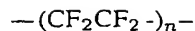
It has a high crystalline melting point (327 °C), very high melt viscosity (10 – 100 GPa · s at 380 °C), and a high maximum use temperature (> 260 °C). In addition, it exhibits unusual toughness down to very low temperatures (< −200 °C); its molecular mass is extremely high ($10^6 - 10^7$). It is insoluble in all known solvents and resists attack by most chemicals. Dielectric loss is low, whereas dielectric strength is high; antistick and antifriction properties are most unusual. Although these properties give PTFE great commercial value, they also rule out processing by conventional thermoplastic techniques.

Polytetrafluoroethylene is produced in three forms: *Granular PTFE* is prepared by suspension polymerization. The coarse product is cut to uniform particle size and processed by powder metallurgy techniques. *Fine powder resins* are prepared by dispersion polymerization and coagulation by high-speed agitation. The fine powder resins consisting of uniform particles of 0.2 μm diameter are mixed with a lubricant such as kerosene and processed by a cold extrusion method called paste extrusion. The third form of PTFE is an *aqueous dispersion*. The dispersion products are processed by latex processing techniques (dip coating or spray coating) followed by baking at high temperature which causes coalescence into a continuous film.

Manufacturers of PTFE resins include Ausimont (Algoflon and Halon), Daikin Kogyo (Polyflon), Du Pont (Teflon), Hoechst (Hostaflon), ICI (Fluon), and the former Soviet Union (Ftoroplast). The People's Republic of China also manufactures PTFE products.

2.2.1. Production

Polymerization. Tetrafluoroethylene must be polymerized with great care to avoid thermal decomposition of the monomer, which can disproportionate explosively to carbon and carbon tetrafluoride:

$$CF_2=CF_2 \longrightarrow C + CF_4 \quad \Delta H = -316.4 \, kJ/mol$$

This reaction, which generates the same explosive force as gun powder, can be initiated by hot spots formed during polymerization. Because of the high heat of polymerization of TFE

and the excellent insulating qualities of the polymer, hot spots can develop if mixing is not adequate or polymerization is not controlled. Therefore, equipment and polymerization vessels must be adequately barricaded to prevent injury or death in the event of monomer decomposition. Polymerization in storage vessels can be prevented by the addition of inhibitors such as terpenes, mercaptans, or amines. However, these must be completely removed from the TFE before use.

Tetrafluoroethylene is polymerized in aqueous medium by two different processes. In the first, little or no dispersing agent is employed and vigorous agitation produces a coagulated granular resin. In the second procedure, a fluorinated surfactant is employed and agitation is very mild, producing small spherical particles dispersed in the aqueous medium. In the latter process, coagulation of the dispersion is avoided until after polymerization is completed. Subsequent precipitation of the particles produces fine powder resins which are converted to finished products by paste extrusion. The dispersion can also be concentrated and stabilized by addition of a nonionic surfactant. These stabilized aqueous dispersions can be applied by spray or dip coating.

Granular Resins. Granular resin was the first commercial PTFE product. The first granular resins were made from pure TFE with no other ingredients except initiator. Currently, however, some granular resins contain traces of certain comonomers such as PPVE [13], [14]. Sometimes granular polymerization is carried out in the presence of a small amount of a dispersing agent. Alkaline buffering agents are used occasionally. In the early stages of granular polymerization, a dispersion is formed, but the polymer soon coagulates. Subsequent polymerization occurs on the solid particles in a gas–solid reaction in which the water acts primarily as a heat-transfer medium. The polymerized product consists of stringy, irregularly shaped particles, which can exceed a millimeter in size. However, the specific surface area of these particles is over $2 \, m^2/g$, which is ca. 1700 times the observed outer surface area. Therefore, the particles must be very porous and spongelike, as is confirmed in photomicrographs.

The "as-polymerized" products cannot be used as such, but must be cut to uniform particle size to provide sinterability. Coarse cut products have good powder flow, but leave a high void content after sintering. Finely cut resins give void-free moldings, but have reduced powder flow. A good compromise between ease of handling and ease of molding is achieved by reducing the particle size to $400-800 \, \mu m$ [15]. For some applications (ram extrusion of tubes and rods), the cut resins are partially presintered for better handling.

Fine Powder Resins. Fine powder resins are produced by polymerizing TFE in the presence of a dispersing agent such as ammonium perfluorooctanoate [16]. The process partially resembles emulsion polymerization. The polymer is highly crystalline and has little ability to solubilize the monomer. In addition, the polymer is insoluble in the monomer, as is typical of an emulsion polymerization. Many of the principles of emulsion polymerization apply to this process. Initially, only pure TFE polymers were prepared in this way, but products containing traces of comonomers such as HFP, CTFE, and PPVE are also made [17], [18]. The properties of these modified fine powders vary with the type and manner of addition of the comonomer.

The dispersion product must not coagulate during polymerization but must be sufficiently unstable to allow coagulation at the end of the polymerization cycle. Very gentle stirring prevents premature coagulation during polymerization. The average particle size is ca. $0.2 \, \mu m$. The specific surface area is ca. $12 \, m^2/g$, which agrees well with calculated values. Unlike the granular products, the dispersion particles display little, if any, porous structure. During the coagulation phase, the nonwettable polymer floats to the surface, where it is drawn off and dried.

Aqueous Dispersions. Aqueous dispersions are made by the same polymerization process used to prepare fine powder resins. The crude dispersions can be polymerized to give different average particle sizes. The most commonly used dispersion has an average particle size of ca. $0.2 \, \mu m$. The "as-polymerized" dispersion must be stabilized and concentrated before use. A nonionic surfactant such as Triton X-100 is normally employed for stabilization. The dispersion
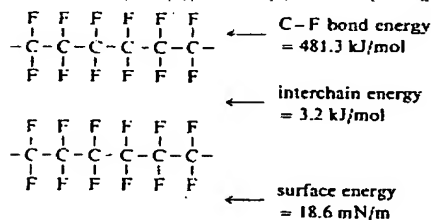
is concentrated thermally to 60–65 % solids. Other additives such as thiotropic agents and fillers may be used to modify the dispersion further.

Filled Resins. A variety of fillers are utilized by PTFE manufacturers and processors; they include glass fibers, graphite, asbestos, molybdenum sulfide, and bronze. Fillers can be blended dry with the PTFE powder before molding or can be coagulated with the dispersion to produce a filled fine powder. The filler serves to improve wear resistance, increase hardness, or reduce creep.

2.2.2. Properties

Physical Properties. The structure of PTFE chains is unusual in that they are completely linear. The branching that occurs during the free-radical polymerization of polyethylene cannot take place during the polymerization of TFE. Furthermore, PTFE chains are stiffer than polyethylene chains because their fluorine atoms are larger than hydrogen atoms. Steric hindrance prevents a PTFE chain from assuming a planar zigzag structure; instead, it is forced to adopt a zigzag structure with a helical twist along the chain axis. Crystals of PTFE are made up of chains with a 180° twist every 13 to 15 carbon atoms, depending on the temperature. The high melting point of PTFE (327 °C) is due to the small entropy change produced during melting, which in turn results from the stiffness of the chains [19].

The chemical bonding forces within the chains, between the chains, and the polymer surface are unusual:

F F F F F F
| | | | | |
–C–C–C–C–C–C–   ← C–F bond energy
| | | | | | = 481.3 kJ/mol
F F F F F F

                                        ← interchain energy
                                              = 3.2 kJ/mol
F F F F F F
| | | | | |
–C–C–C–C–C–C–
| | | | | |
F F F F F F
                                        ← surface energy
                                              = 18.6 mN/m

The C–F bond energy is among the highest known. However, the interchain bonding forces are very weak, and the surface energy is very low. This combination of unusually strong and weak forces results in many unique properties.

The melting point of once-melted PTFE is 327 °C, but high molecular mass, virgin unmelted PTFE melts at a higher temperature (342 °C). Differential scanning calorimetry (DSC) indicates that the 342 °C melting point is irreversible and the subsequent melting point is 327 °C. Electron-microscopic studies of dispersion particles indicate that the rodlike crystals in virgin PTFE are fully extended with few defects [20]. Virgin PTFE particles are 92–98 % crystalline. The crystallinity of once-melted PTFE varies with molecular mass and the rate of cooling from the melt. However, commercial grades are usually 45–75 % crystalline.

The molecular mass of PTFE cannot be determined by the usual methods that require dissolution of the polymer because there is no known solvent for PTFE below 300 °C. However, the number-average molecular mass has been estimated from the determination measurements of end groups. Because the molecular mass of PTFE is very high, the concentration of end groups is very low. A quantitative method must be sensitive to less than 1 ppm of end groups. An elegant method tags the end groups with radioactive sulfur in the initiator [21]; the sulfur from the initiator must be retained in the polymer with no loss by hydrolysis. When persulfate is used as the initiator, the resulting sulfate end groups are hydrolyzed to carboxylic acid end groups and no radioactive sulfur is detected in the polymer. However, when an iron–bisulfite initiator is used, the sulfur is retained in the polymer because the initiating species (a bisulfite radical, $HOSO_2\cdot$) gives rise to hydrolytically stable sulfonic acid end groups.

A series of polymers was prepared, using the radioactive bisulfite–iron initiator, with molecular masses in the range of industrial interest. The number-average molecular masses were calculated from the radioactive sulfur content, assuming two sulfonic acid groups per polymer chain. The calculated molecular mass ranged from $3\cdot89 \times 10^5$ to $8\cdot9 \times 10^6$. These samples were used to calibrate other methods for measuring the molecular mass of PTFE resins, such as the standard specific gravity (SSG) method [22]. Since the rate of crystallization varies inversely with molecular mass, samples of high molecular mass have a lower SSG than those

of low molecular mass; typical values for polymers of commercial interest range from 2.14 to 2.20. The SSG method is widely used with PTFE resins. The correlation between number-average molecular mass $\bar{M}_n$ and the SSG is given by the following relationship:

$$SSG = 2.612 - 0.058 \log_{10} \bar{M}_n$$

Studies on the melting behavior of virgin PTFE by DSC [23] has led to another method for measuring molecular mass. The following relationship was found between number-average molecular mass and heat of crystallization (ΔH_c, J/g):

$$\bar{M}_n = 2.1 \times 10^{10} \cdot \Delta H_c^{-5.16}$$

In addition to its crystalline melting point at 327 °C, PTFE has several transition temperatures [19]. Two crystalline transitions, at 19 and 30 °C, have a significant effect on product behavior. Below 19 °C, the polymer crystallites exist in an almost perfect three-dimensional array. Above 19 °C, the triclinic unit cell changes to a hexagonal unit cell. Slight untwisting of the chains is observed in the cell from 13 CF_2 groups to 15 CF_2 groups per 180° twist. The transition at 30 °C is only ca. one-tenth as large as that at 19 °C. The hexagonal unit cell disappears above 30 °C, but the rodlike hexagonal packing of the chains in the lateral direction is retained. As measured by torsion pendulum, two important amorphous transitions occur at ca. −97 °C and +127 °C, these transition temperatures are dependent on frequency. The lower transition ranges from −110 to −73 °C when measured at frequencies from 0.033 to 90 Hz. The higher temperature transition ranges from 120 to 140 °C over the same frequency range.

Mechanical Properties. The mechanical properties of PTFE are affected by processing variables such as preform pressure, sintering temperature, and cooling rate, as well as by polymer variables such as molecular mass, particle size, and particle-size distribution. Properties affected are the flex life, tensile strength, elongation, permeability, stiffness, resilience, and impact strength. Properties such as the coefficient of friction, low-temperature flexibility, and thermal stability are relatively unaffected. Typical values for the mechanical properties of

granular and fine powder PTFE resins are listed in Table 2. Further data are given in [24–26].

The crystalline transition at 19 °C causes a volume change of 1.0 – 1.8 % and must be taken into account when precision parts made from PTFE are designed.

The coefficient of friction of PTFE is unusually low. Static friction decreases with increasing load and is less than the dynamic friction which frees PTFE from stick – slip problems. Because of the low surface energy, only liquids with extremely low surface tension (e.g., perfluorocarbon acids) can wet a PTFE surface. Surfaces can be made wettable by treatment with alkali-metal compounds (e.g., sodium naphthenate) which, however, also increases the coefficient of friction.

The effect of fillers on the mechanical properties of PTFE is shown in Table 3; tensile strength, elongation, and the coefficient of friction are not significantly affected. In contrast, wear resistance is dramatically improved: the wear factor of the bronze-filled material is only 1/250th that of unfilled PTFE.

Electrical Properties. The very low dielectric constant of PTFE (2.1) does not change over a wide range of temperature (−40 to +250 °C) and frequency (5 Hz to 10 GHz). Such electrical behavior is attributed to PTFE's highly symmetrical structure composed solely of carbon–fluorine bonds, in which all electrical dipoles are exactly balanced. Similarly, the dissipation factor is extremely low and independent of temperature or frequency. Resistivity and dielectric strength, on the other hand, are very high, as is arc resistance; PTFE leaves no carbonized path. The electrical properties of PTFE are given in Table 4.

Electrical properties can be adversely affected by voids, which may reduce the dielectric strength and corona resistance of fabricated parts. Voids must be minimized to achieve optimum electrical insulation.

Chemical Resistance. Polytetrafluoroethylene is resistant to attack by most chemicals, including aqua regia, hot fuming nitric acid, hot caustic, gaseous chlorine, chlorosulfonic acid, organic esters, ketones, and alcohols. The only materials known to attack PTFE are molten alkali metals, chlorine trifluoride, and gaseous

Table 2. Mechanical properties of PTFE resins

Property	Granular	Fine Powder	ASTM
Tensile strength, MPa	7 – 28	18 – 24	D 638
Elongation, %	100 – 200	300 – 600	D 638
Flexural modulus, MPa	350 – 630	280 – 630	D 747
Flexural strength, MPa	no break		D 790
Impact strength, J/m	160		D 256
Compressive stress			
at 1 % deformation, MPa	4.2		D 695
Hardness, Shore D	50 – 65	50 – 65	D 1706
Coefficient of thermal			
expansion, K^{-1}	12×10^{-5}		D 696

Table 3. Properties of unfilled and filled PTFE resins

Property	Unfilled resin	Filled resin	
		25 % glass	60 % bronze
Relative density	2.18	2.24	3.74
Tensile strength, MPa	28	18	14
Elongation, %	350	250	150
Impact strength, J/m	152	119	
Hardness, Shore D	51	57	70
Wear factor, mPa^{-1}	5013	26.2	12
Coefficient of friction			
Static, 3.4 MPa load	0.08	0.13	0.10
Dynamic, $u=900$ m/s	0.01	−0.24	−0.22
Thermal conductivity, $mW\ m^{-1}\ K^{-1}$	0.24	0.45	0.46

Table 4. Electrical properties of PTFE resins

Property	Granular	Fine powder	ASTM
Dielectric constant,			
60 Hz to 2 GHz	2.1	2.1	D 150
Dissipation factor,			
60 Hz to 2 GHz	0.0003		D 150
Volume resistivity,			
$\Omega \cdot cm$	$>10^{18}$	$>10^{18}$	D 257
Surface resistivity,			
Ω/m^2	$>10^{16}$		D 257
Surface arc resistance, s	>300	>300	D 495
Dielectric strength,			
2-mm thickness, kV/mm	23.60	23.60	D 149

fluorine at elevated temperature and pressure. Some highly fluorinated oils can swell or dissolve PTFE near its melting point. A list of chemicals that are compatible with PTFE is available [27].

Flame Resistance. Polytetrafluoroethylene is one of the most flame-resistant polymers known and does not support combustion in air. It has an extremely high limiting oxygen index (LOI) of 96 %, i.e., it burns only in almost pure (96 vol%) oxygen.

Weatherability. The weatherability of PTFE is remarkable; it is completely unaffected by all types of weather from dry desert heat to humid jungle conditions. Test films showed no change after 20 – 30 years of continuous exposure in Florida.

Radiation Resistance. On exposure to a high-energy electron beam or gamma radiation, PTFE undergoes degradation rather than cross-linkage. In the absence of oxygen, stable radicals are produced which slow down the rate of degradation. However, in the presence of air,

the radicals react with oxygen which accelerates scission and degradation. On exposure to 10^4 Gy (1 Mrad) of radiation in air, PTFE loses 50 % of its original tensile strength. Irradiation also affects its electrical properties: resistivity decreases, whereas the dielectric constant and dissipation factor increase.

Thermal Stability. In both air and nitrogen, PTFE has an extremely high thermal stability. Rates of decomposition are not measurable below ca. 440 °C, decomposition rates are high at 540 °C. In vacuum pyrolysis of thin films, first-order thermal decomposition occurs, the TFE monomer being the main product [28]; the activation energy is 347.4 kJ/mol. The melt viscosity decreases during pyrolysis which probably involves random chain cleavage followed by depolymerization (short kinetic chain length) and termination by disproportionation.

2.2.3. Processing

Granular Resins. Moldings are produced from granular resins in three steps: First, the dry powder is placed in a mold and compressed at moderate temperature to produce a preform that is strong enough for handling without breaking. The preform is than placed in an oven at 380 °C to allow the particles to coalesce. This operation is called sintering. The final step is controlled cooling to produce the desired crystallinity. Granular resins are available in a number of forms that are optimized for different types of molding. High-flow resins are used in small and automatic moldings. Finely divided resins are preferred for large billet moldings to which they impart superior properties. Presintered resins are easier to handle and are preferred in ram extrusion applications. Most PTFE manufacturers give detailed descriptions of molding equipment and procedures [29].

Automatically molded articles require no further finishing after molding. However, large billets and rods are subsequently skived or machined. Film and sheet are produced by skiving a billet on a lathe. Precision parts can be machined from ram-extruded rods. Another method, called coining, is used for articles that are too complicated to make by machining. In this operation, a sintered molding is heated to the melting point, quickly pressed into a mold cavity, and held under pressure until it resolidifies. Coined moldings are limited in their upper service temperature. After long periods at high temperature, they return to their original precoining shape.

Fine Powder Resins. The paste-extrusion process for fine powder resins represented an important advance in PTFE processing. It permits the manufacture of continuous PTFE tubing and continuous PTFE coatings on wires.

In paste extrusion, 15 – 25 wt % of lubricant (a petroleum fraction, usually kerosene) is mixed with the fine powder resin. The wetted powder is then gently shaped into a preform at low pressure. (Fine powder resins are extremely sensitive to shear; great care must be taken to avoid shearing the powder before extrusion, otherwise processibility may be lost.) The preform is forced through a die mounted in the extruder. The high shear exerted at the die fibrillates the powder and confers "green strength" to the extrudate. The lubricant is then evaporated and the extrudate is sintered at 380 °C to coalesce the elongated particles. Drying and sintering are performed consecutively by passing the extrudate through a multistage oven located directly after the extruder. Residence time in the oven can vary from a few seconds for thin-walled wire insulation to a few minutes for large-diameter tubing. Extrusion pressure depends on the reduction ratio, the extrusion rate, the lubricant content, and the extruder characteristics.

Paste extrusion is also used to produce unsintered tape. Lubricant mixing and extrusion are the same as above. The product is extruded into rods, which are calendered on hot rolls to the desired dimensions.

Different fine powder resins have been developed for different applications. Powders that are suitable for high reduction-ratio applications, such as wire coatings, are not usually suitable for medium reduction-ratio applications such as tubing. (The reduction ratio is the ratio of the die diameter to the product diameter.) Thread sealant tapes are generally produced with other special grades. New types of fine powder resins are constantly being developed, leading to both improved and new applications and processing techniques [30–32].

Dispersion Resins. In general, PTFE dispersions are concentrated to 50–60 % solids and stabilized by a nonionic surfactant. The dispersions are applied to various substrates by spraying, flow-coating, dipping, coagulating, or electrodepositing. Films can be made by casting the aqueous dispersion on a supporting surface, drying, baking, and cooling. If the film is too thick, cracks develop; the maximum film thickness per application is ca. 40 μm. Thicker coatings are made by casting and baking a series of layers.

An important application of PTFE dispersions is cloth impregnation. The woven cloth (e.g., fiber glass) is usually dipped into the dispersion and dried and sintered as in film formation. In some cases, the fiber is coated with the PTFE dispersion before weaving. Dispersions are also used in the production of PTFE fibers [33]. The dispersion is mixed with a matrix-forming medium such as viscose and spun into fibers through a spinneret and coagulating bath. The fibers are heated to remove the matrix polymer, sintered, and drawn for spinning.

2.2.4. Uses

About half of the PTFE resin that is produced is used for electrical purposes [34]. A major application is PTFE-insulated hookup wire used in military and aerospace electronic equipment. Polytetrafluoroethylene is also used in coaxial cables wrapped with PTFE tape, as insulation for airframe and computer wires, as well as in electrical components and "spaghetti" tubing.

Other important uses of PTFE resin are found in fluid-conveying systems, where it is used for gaskets, molded packings and seals, piston rings, bellows, overbraided hose, and lined pipe. Laboratory apparatus is also made of PTFE.

In static and dynamic load supports, large quantities of PTFE are used for bearings, ball- and roller-bearing components, and sliding bearing pads. The most commonly use known is as a release coating; PTFE-coated cookware utilizes a large amount of resin each year. Sheet and pressure-sensitive tape also serve for release applications.

Architectural fabrics are made by coating heavy-duty glass fabric with PTFE dispersions. These materials have outstanding weatherability and are resistant to chemicals, microorganisms, and fire. They have been used to enclose football stadiums and shopping centers.

Fibers and filaments are used in the production of PTFE filter cloth. Highly porous fabrics (e.g., Gore-Tex) are prepared by a process based on the fibrillation of high molecular mass PTFE. These fabrics have a high permeability for water vapor, but none for liquid water. They are widely used in outdoor wear and camping accessories.

A small but important use for PTFE is in medicine [35]; due to its inert and antiadhesive character, it is a highly suitable material for implants in the human body.

The main uses of the principal commercial PTFE resins are given in Table 5.

Table 5. Uses of PTFE resins

Type of resin	Uses
Granular	
Agglomerates	Gaskets, packing, seals, bearings, sheet, rod, heavy wall tubing, and tape
Coarse cut	Tape, molded shapes for chemical, mechanical, electrical, and nonstick applications
Fine cut	Molded sheets, tape, wire, wrapping, tubing, and gasketing
Presintered	Rods and tubes
Fine powder	
High reduction ratio *	Wire coating and thin-walled tubing
Medium reduction ratio *	Tubing, pipe, overbraided hose, and spaghetti tubing
Low reduction ratio *	Thread-sealant tape, pipe liners, tubing, and porous structures
Dispersion	
General purpose	Impregnation, coating, and packing
Coating	Film and coating

* Ratio of extrusion-die diameter to product diameter.

2.3. Tetrafluoroethylene– Hexafluoropropylene Copolymers

Copolymers of tetrafluoroethylene (TFE) and hexafluoropropene (HFP) are commonly referred to as fluorinated ethylene–propylene (FEP) resins [25067-11-2]. They are linear, perfluorinated copolymers:

$$-[(CF_2CF_2)_xCF_2CF]_y-$$
$$\qquad CF_3$$
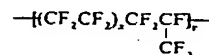
The presence of HFP in the polymer chain reduces the tendency to crystallize. Thus, a copoly-